Performance of MAX phase Ti$_3$SiC$_2$ under the irradiation of He/H :

Elaboration from DFT

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Materials Issues

Neutron flux (14MeV, 0.5-0.8 MW/m²)
Heat flux (>10MW/m² for some spikes)
Neutron activation (half life of resultant nuclei)
Displacement Cascades and Damage (up to 1-100 dpa)
Erosion by Sputtering
  - Neutron Irradiation
  - Plasma Wall Interaction (~10 keV D, T, He)
Plasma Stability
  - Edge-localised modes and plasma disruptions
Tritium retention
For the structural material
  - Mechanical properties
Current Materials for ITER

- Tungsten
- Beryllium
- Carbon
Materials Challenges

Novel materials with high performance for high temperature, high radiation environments

Motivation!!
MAX phase:

- M is an early transition metal
- A a group III or IV element
- X either C or N
Desirable Characteristics of Ti$_3$SiC$_2$

- High melting point
- Tolerant to irradiation damage
- Not retain too much hydrogen or helium
- Good thermal and electrical conductor
- Low cost
- No long lived radioactive isotopes from neutron irradiation
- Ideally composed of low atomic number species
- Low sputtering yield
- Easy to machine and join
- Good electrical and thermal conductor
- High resistance to thermal shocks
- Good thermomechanical properties
Evaluate the performance from chemical bonds pointview using DFT, especial focused on the retention and mechanical properties under the irradiation of He/H
Modeling methods

• DFT (CASTEP code)
• Total energies: the plane-wave pseudo-potential method;
• The electron–ion interactions: the norm-conserving pseudo-potentials;
• The exchange–correlations: the generalized gradient approximation (GGA-PW91);
• The cutoff energy of the plane-wave basis set: 670 eV;
• The Brillouin-zone (BZ) sampling: a 5X9X2 k-mesh (within the Monkhorst–Pack scheme);
• The electron self-consistency: 2.0X10^5 eV/atom.
$\text{Ti}_3\text{SiC}_2$: Layered structure; Space group: p63/mmc
Solution of He/H

<table>
<thead>
<tr>
<th></th>
<th>$E_{He}^s$ (eV)</th>
<th>$\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He in I-Ti</td>
<td>5.10</td>
<td>0.72%</td>
</tr>
<tr>
<td>He in I-SiTi</td>
<td>3.11</td>
<td>0.79%</td>
</tr>
<tr>
<td>He in I-SiC</td>
<td>2.99</td>
<td>0.62%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$E_{H}^f$ (eV)</th>
<th>$\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H in I-Ti</td>
<td>-2.228</td>
<td>1.45%</td>
</tr>
<tr>
<td>H in I-SiTi</td>
<td>-2.850</td>
<td>0.90%</td>
</tr>
<tr>
<td>H in I-SiC</td>
<td>-2.853</td>
<td>0.55%</td>
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</tbody>
</table>

Cleavage characteristics in the presence of He/H

Cleavage will start from the Si-Ti interlayer.
Critical stress of cleavage fracture (GPa)

<table>
<thead>
<tr>
<th></th>
<th>He-SiTi</th>
<th>He-Ti</th>
<th>He-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect crystal</td>
<td>10.06</td>
<td>20.23</td>
<td>13.53</td>
</tr>
<tr>
<td></td>
<td>26.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cleavage also starts from the Si-Ti interlayer in the presence of H/He.

Partial density of states

Hydrogen-free in Ti$_3$SiC$_2$

Hydrogen in I-SiTi

The key: p-d hybridization between Ti2 and Si atom
|                      | Charge (|e|)                  | Overlap population (|e|) | Bond lengths (Å)                  |
|----------------------|---------------------------|-------------------------|----------------------------------|
| **H-free**           | -0.01(Si\(^A\))          | 0.77(Si\(^A\)-Ti\(^A\))| 2.667(Si\(^A\)-Ti\(^A\))        |
|                      | -0.01(Si\(^B\))          | 0.77(Si\(^B\)-Ti\(^B\))| 2.667(Si\(^B\)-Ti\(^B\))        |
|                      | 0.36(Ti\(^A\))           | -0.08(Si\(^A\)-Ti\(^B\))| 2.668(Si\(^A\)-Ti\(^B\))        |
|                      | 0.36(Ti\(^B\))           |                         |                                  |
| **H in I-SiTi**      | -0.29 (H)                | 0.38 (H-Si\(^B\))      | 1.915 (H-Si\(^B\))              |
|                      | -0.03 (Si\(^A\))         | 0.73 (Si\(^A\)-Ti\(^A\))| 2.661 (Si\(^A\)-Ti\(^A\))        |
|                      | -0.02 (Si\(^B\))         | 0.42 (Si\(^B\)-Ti\(^B\))| 2.759 (Si\(^B\)-Ti\(^B\))        |
|                      | 0.37 (Ti\(^A\))          | -0.18 (Si\(^A\)-Ti\(^B\))| 2.830 (Si\(^A\)-Ti\(^B\))        |
|                      | 0.50 (Ti\(^B\))          |                         |                                  |
| **H in I-SiC**       | -0.19 (H)                | 0.19 (H-Si\(^A\))      | 2.108 (H-Si\(^A\))              |
|                      | 0.05 (Si\(^A\))          | 0.35 (H-Ti\(^B\))      | 2.045 (H-Ti\(^B\))              |
|                      | 0.01 (Si\(^B\))          | 0.77 (Si\(^A\)-Ti\(^A\))| 2.697 (Si\(^A\)-Ti\(^A\))        |
|                      | 0.38 (Ti\(^A\))          | 0.76 (Si\(^B\)-Ti\(^B\))| 2.741 (Si\(^B\)-Ti\(^B\))        |
|                      | 0.42 (Ti\(^B\))          | **-0.57 (Si\(^A\)-Ti\(^B\))** | 2.792 (Si\(^A\)-Ti\(^B\))        |
Good: H ; Bad: He?
Experiment results by other groups

(a) TEM micrograph taken under kinematic imaging conditions off from the central [100] beam direction (SAED in b) and underfocused by 1 nm obtained from Ti3AlC2 irradiated with a 200 keV He+ ion fluence of 2·10^17 ions cm^2 at 500°C; (c) TEM micrograph in the as-focused condition; (d) TEM micrograph in low-magnification showing a uniform band of dark contrast at 0.79 nm, as predicted for the peak intensity of He concentration by SRIM calculations. SAED patterns, with insets showing corresponding high-resolution STEM HAADF micrographs obtained from the following respective areas of the sample: (e) near-surface region of the sample, (f) within the darker contrast band corresponding to stopping of He atoms and (g) the pristine region.

(b) Corresponding the cross-section bright-field TEM images of irradiated Ti3AlC2, increasing Temperature (500°C)

(d) The bright-field TEM image of the Ti3AlC2 irradiated at RT with doses 1.0×10^{18} ions cm^2

*Scripta Materialia 77 (2014) 1–4*
Designing novel materials with high tolerance to H/He irradiation

Si self-repair behavior from damage to recombination under helium irradiation and subsequent annealing

Active A layer

Acta Mater. 97 (2015) 50
Ti$_3$SiC$_2$ exhibits different mechanical response to H and He doping because of different electronic hybridization behaviors. Chemical bonding of impurities in Ti$_3$SiC$_2$ always determines the cleavage behavior.

Hydrogen hybridizes with s states of Si. The interaction between He and lattice atoms is primarily elastic (closed shell electronic structure of He). He prefers staying near Si planes, whereas at the expense of pushing nearby Si atom out of its lattice position.

Helium provokes fracture failure through the Si–Ti layers. The critical stress of cleavage fracture in the presence of He decreases by almost 62.5% of the pristine crystal, which however have not occurred in the presence of H.

The activity of Si atoms endows the Si layers with a self-repair ability in response to helium irradiation and to act as channels for the accommodation of helium at all temperatures and for its desorption and transport at high temperatures.

Prediction: small retention of H in Ti$_3$SiC$_2$

The exotic properties inherent in Ti$_3$SiC$_2$ (self-repair) is an important to provide a clue to design an advanced material for use in fusion reactor.
Acknowledgements

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Thanks for your attention!